

# Performance of the Semiempirical PM3 (tm) Method in the Geometry Optimization of Transition Metal Complexes

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**ABSTRACT:** The geometries of three different sets of transition metal compounds are optimized with the semiempirical PM3 (tm) method. The systems under test are: (i) products of cyclometallation, like  $[\text{Pd}\{\text{C}_6\text{H}_4[\text{CH}(\text{Me})\text{NH}_2]\}\text{Br}(\text{PPh}_3)]$ , (ii) molecular dihydrogen complexes, like  $[\text{W}(\text{CO})_3(\text{H}_2)(\text{PR}_3)_2]$ , and (iii) H-BR<sub>2</sub>  $\sigma$  complexes of titanium, like  $\text{TiCp}_2(\text{HBcat})_2$  (cat = O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>). The results are compared with available X-ray and neutron diffraction data, as well as with *ab initio* molecular orbital and density functional theory results published in the literature. The performance of the PM3 (tm) method ranges from excellent in the case of dihydrogen complexes to very poor in the case of H-BR<sub>2</sub> complexes. © 2000 John Wiley & Sons, Inc. *J Comput Chem* 21: 562–571, 2000

**Keywords:** semiempirical methods; PM3 (tm); coordination complexes; organometallic compounds; geometry optimization

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## Introduction

Despite the ever growing power of modern computers, the study of the reactivity of transition metal complexes continues to demand a large, sometimes prohibitive, amount of computer time. The reason for this high computational cost is double. On one hand, transition metal complexes are usually large, the computer cost increasing sharply with the size of the system. On the other hand, the study of these species, because of their chemical complexity, requires quite often high level computational methods, with approaches like the Hartree–Fock (HF) or the local density functional theory (local DFT) being seldom sufficient.

Not surprisingly, practical calculations on transition metal systems try to circumvent one of these two problems. The answer to the problem of size is modelization. The calculation is not carried out on the real system, but on a simplified version of it. In this way, all  $\text{PR}_3$  phosphines are considered to be  $\text{PH}_3$ , all  $\text{C}_5\text{R}_5$  cyclopentadienyl rings are considered to be  $\text{C}_5\text{H}_5$ , and so on. This approach is indeed successful in a number of examples,<sup>1–3</sup> but has an intrinsic inaccuracy in the description of the steric and electronic effects of the ligands.<sup>4</sup> Recent methodological developments in this field involve hybrid methods using different descriptions for different parts of the same molecule. The IMOMM scheme, combining quantum mechanics and molecular mechanics,<sup>5</sup> is certainly successful in a number of cases for the introduction of steric effects,<sup>6</sup> and the ONIOM approach,<sup>7</sup> combining different levels of quantum description, aims to do the same in terms of electronic effects. At any rate, the high-level calculation on the model system is still computationally demanding, and one may wonder if there are better alternatives.

The second major venue to the practical performance of calculations on transition metal complexes is the use of semiempirical methods. After all, methods such as MNDO,<sup>8</sup> AM1,<sup>9</sup> or PM3<sup>10</sup> are orders of magnitude cheaper than their *ab initio* and most of the DFT counterparts, and have been extremely productive in the field of theoretical organic chemistry. However, parametrization of these methods for transition metal systems is not trivial. Some attempts have, nevertheless, been made to introduce *d*-orbitals in the traditional semiempirical methods, and one can mention MNDO/*d*,<sup>11,12</sup> SAM/1,<sup>13,14</sup> PM3-*d*,<sup>15</sup> ZINDO,<sup>16,17</sup> and EHMO-ASED.<sup>18</sup> None of these methods has, however, reached a widespread use, maybe because of poor distribution of

the codes. Things may be currently changing with the appearance of the PM3 (tm) method.<sup>19,20</sup>

The PM3 (tm) method, which has recently been developed,<sup>19,20</sup> is distributed with the Spartan suite of programs,<sup>21</sup> and features a parameter set for a number of transition metals. Cundari and Deng<sup>22</sup> have recently published an analysis of the accuracy of this method in the optimization of geometries of a number of transition metal complexes. According to their results, the agreement of the predicted geometries with the experimental data is good, especially in the case of early transition metals, and it can be compared to more expensive methods such as MP2. There are some other articles comparing PM3 (tm) with *ab initio* or molecular mechanics methods in concrete systems: Lindoy et al.<sup>23</sup> tested its performance on the geometry optimization of a set of nickel complexes with tetrazamacrocycles, and found that PM3 (tm) results were reasonable, although they could not beat those of a force field specifically designed for those systems. Børve et al.<sup>24</sup> evaluated its proficiency on a number of systems relevant to the homogeneous catalysis of olefin polymerization, and found a good performance in terms of geometries, and a poor performance in terms of energetics. This result is not surprising, because this method has been parametrized for geometries, but not for heats of formation, dipole moments, or ionization potentials.<sup>20</sup> Muñoz Escalona and coworkers<sup>25</sup> used this method to study the ethylene polymerization catalyzed by zirconocene derivatives, and found a good agreement in both the geometries and energy of the different species, compared with the previously published work using *ab initio* methods, while Dobrowolski et al.<sup>26</sup> compared the method with DFT and RHF in the study of dioxygen complexes. Klobukowski and coworkers<sup>27</sup> found that the accuracy of PM3 (tm) is higher than that of HF-SCF and local DFT methods but inferior to nonlocal DFT for dinuclear manganese carbonyl compounds, and Cundari et al.<sup>28</sup> stated that molecular mechanics outperforms PM3 (tm) in the modeling of vanadium oxo complexes. On the other hand, some articles dealing with the application of the method to experimental problems have been published, such as the dynamic behavior of a platinadehydrobenzo[19]annulene,<sup>29</sup> or the importance of electronic and steric effects in cyclopalladated derivatives of ferrocene.<sup>30–32</sup>

In this article, we present a test of the performance of the PM3 (tm) method on a number of different types of transition metal complexes. After a section describing the computational details, one section is devoted to each type of species, and the

article finishes with some general remarks about the usefulness of this technique.

## Computational Details

The calculations were performed with the Spartan suite of programs.<sup>21</sup> The PM3 (tm) method<sup>19,20</sup> was used with the default parameters supplied by the program. No symmetry was used, and no geometrical restrictions were imposed. Conformer searches were carried out with the Osawa method.<sup>33</sup>

A few single-point DFT calculations are also presented. These DFT calculations were done at the SVWN level<sup>34</sup> using the basis set labeled as DN\* in the program.<sup>21</sup> This is a numerical basis set that incorporates polarization function on the nonhydrogen atoms.

## Results and Discussion

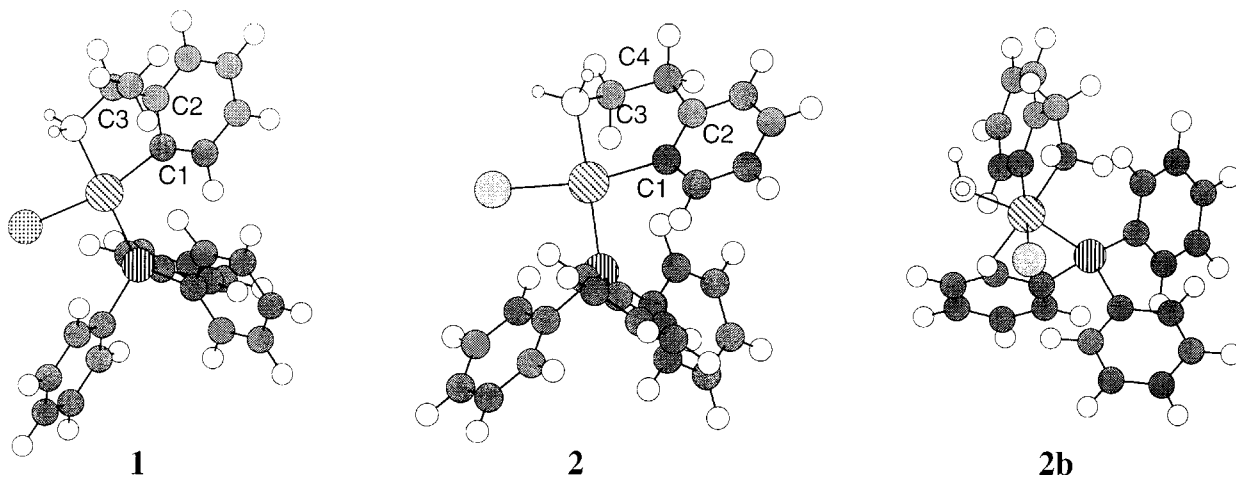
### GEOMETRIES OF CYCLOMETALLATION PRODUCTS

The selective and controlled activation of C—H bonds is one of the main goals of the organometallic chemistry. One of the easiest ways to achieve it is through a cyclometallation reaction that can be viewed as the formation of a bond between a metal and an atom attached to one of its ligands, therefore giving rise to a product with a cycle that includes the metal atom. This type of reaction has been the subject of a great deal of research.<sup>35–38</sup> In particular, complexes containing N-donor ligands

have been examined in detail from an experimental point of view. The factors ruling their behavior are not fully understood yet, and theoretical calculations on this subject might be helpful. We are indeed working on such a project. The large size of the systems, as well as the complex mixture of electronic and steric factors makes them a good candidate for use of the PM3 (tm) method. We report here the results of the geometry optimizations of three different compounds, and compare them with experimental X-ray data.

Three different complexes are considered:  $[\text{Pd}\{\text{C}_6\text{H}_4[\text{CH}(\text{Me})\text{NH}_2]\}\text{Br}(\text{PPh}_3)]$  (**1**),<sup>39</sup>  $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{CH}_2\text{NH}_2)\}\text{Br}(\text{PPh}_3)]$  (**2**),<sup>40</sup> and  $[\text{Mn}\{\text{C}_6\text{H}_2(\text{OCH}_3)_2\text{-4,6-CH}_2\text{NMe}_2\}(\text{CO})_4]$  (**3**).<sup>41</sup> The central atom is palladium—the most widely used metal in this kind of systems—for complexes **1** and **2**, while **3** is a manganese derivative. On the other hand, the metallacycle is a five-membered ring for **1** and **3**, while it is a six-membered ring for **2**. In this way, we try to cover a variety of cases.

The geometry optimization of **1** at the PM3 (tm) level results in the structure shown in Figure 1. Some of the bond lengths and angles are collected in Table I, together with the corresponding X-ray data.<sup>39</sup> The environment of the palladium atom is well reproduced: the largest absolute error is in the Pd—N bond, where the computed length is 0.097 Å shorter than the experimental value. The calculated Pd—C bond length is somewhat larger (by 0.042 Å) than in experiment, but the reproduction of the Pd—P and Pd—Br bond lengths is good. As for the other bonds in the metallacycle, the worst agreement is in the N—C(3) bond, the calculation yielding a value 0.048 Å larger than that from X-ray.



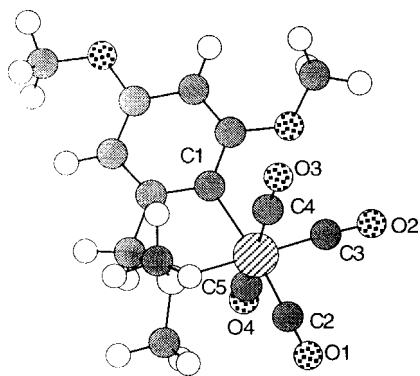
**FIGURE 1.** PM3 (tm) optimized geometry of complexes  $[\text{Pd}\{\text{C}_6\text{H}_4[\text{CH}(\text{Me})\text{NH}_2]\}\text{Br}(\text{PPh}_3)]$  (**1**),  $[\text{Pd}\{\text{C}_6\text{H}_4(\text{CH}_2\text{CH}_2\text{NH}_2)\}\text{Br}(\text{PPh}_3)]$  (**2**), and the artificially lower energy geometry of complex **2** (**2b**).

**TABLE I.**  
Comparison between Experimental and Optimized Bond Lengths (Å) and Angles (°) for Complexes [Pd{C<sub>6</sub>H<sub>4</sub>[CH(Me)NH<sub>2</sub>]}Br(PPh<sub>3</sub>)] (1) and [Pd{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)}Br(PPh<sub>3</sub>)] (2).

	Complex 1		Complex 2	
	Exp.	Calc.	Exp.	Calc.
Pd—C(1)	2.019	2.061	2.004	2.097
Pd—N	2.092	1.995	2.132	2.010
Pd—P	2.244	2.247	2.266	2.248
Pd—Br	2.519	2.502	2.568	2.501
N—C(3)	1.475	1.523	1.464	1.508
C(3)—C(2)	1.504	1.507		
C(3)—N—Pd	110.6	110.4	119.5	96.94
C(1)—Pd—N	81.2	85.7	88.0	82.2
C(1)—Pd—P	93.3	95.0	91.7	95.6
N—Pd—P	172.0	179.2	164.6	178.1
C(1)—Pd—Br	168.5	166.0	166.5	168.8
N—Pd—Br	88.8	80.3	86.0	82.6
P—Pd—Br	97.2	99.0	97.4	95.6

The calculated C(phosphine)—P bond lengths are also larger than the experimental ones. As for the angles, the largest errors in the Pd environment are in the N—Pd—P angle, which is closer to 180 degrees in the calculation, and the N—Pd—Br angle, too small in the calculations. The bite angle of the chelating ligand is 81.2° in the experimental geometry, and 85.7° in our calculations.

The optimized geometry of **2** is depicted in Figure 1, and Table I compares selected bond lengths and angles with experimental data. This system contains a six-membered ring, instead of the five-membered ring of **1**. The presence of the six-membered ring introduces an additional dif-



**FIGURE 2.** PM3 (tm) optimized geometry of complex [Mn{C<sub>6</sub>H<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>-4,6-CH<sub>2</sub>NMe<sub>2</sub>}(CO)<sub>4</sub>] (**3**).

ficulty to the computational reproduction of the experimental geometry because of the greater flexibility associated with this ring. Consequently, in this case the largest errors in the immediate metal environment are again in the Pd—N and Pd—C bond lengths, with discrepancies with experiment of 0.122 and 0.093 Å, respectively (to be compared with values of 0.097 and 0.042 Å for **1**). The discrepancies in the angles are also larger, mainly in the N—Pd—P angle, which is near 180° in the calculated geometry, while in the X-ray structure it is only 164°. A more serious difference appears in the C(3)—N—Pd angle: it has a value of only 96.94° in the calculation, while the experimental value is 119.5°.

To avoid restricting ourselves to complexes containing palladium, complex **3**, where the metal is manganese, was also computed. Pfeffer et al.<sup>41</sup> have prepared this compound, and its crystal structure has been determined. Figure 2 shows the optimized geometry. The comparison between calculated and experimental geometrical parameters (Table II) shows the very good agreement between them: the largest error in bond lengths is only 0.039 Å, corresponding to Mn—N. The calculated

**TABLE II.**  
Comparison between Experimental and Optimized Bond Lengths (Å) and Angles (°) for Complex [Mn{C<sub>6</sub>H<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>-4,6-CH<sub>2</sub>NMe<sub>2</sub>}(CO)<sub>4</sub>] (**3**).

	Experimental	Calculated
Mn—C(1)	2.071	2.081
Mn—C(4)	1.846	1.867
Mn—C(2)	1.818	1.805
C(2)—O(1)	1.151	1.171
Mn—N	2.149	2.110
Mn—C(3)	1.785	1.785
Mn—C(5)	1.831	1.865
C(3)—O(2)	1.159	1.170
C(5)—O(4)	1.149	1.159
C(1)—Mn—N	78.9	80.2
C(1)—Mn—C(3)	96.2	98.2
C(1)—Mn—C(5)	87.6	85.9
N—Mn—C(3)	174.4	176.7
N—Mn—C(5)	90.5	90.9
C(4)—Mn—C(2)	95.7	93.6
Mn—C(3)—O(2)	176.4	176.6
Mn—C(5)—O(4)	174.0	172.3
C(1)—Mn—C(2)	171.9	172.5
N—Mn—C(4)	94.9	95.3
N—Mn—C(2)	93.1	92.7
C(4)—Mn—C(3)	87.4	84.6

Mn—C distances corresponding to CO *trans* to CO tend to be slightly longer than the corresponding experimental values, while in the CO *trans* to Ph the calculated distance is slightly shorter. The angles are also well described; the CO ligands tend to be slightly bent in the calculation, but the largest error in such angles is only 2.8°.

In summary, the agreement between computed and experimental geometries appears to be quite satisfying, especially in the case of five-membered rings, and therefore, the method holds promise for application to these systems, at least for geometry optimizations. In any case, one must be always aware of its limitations, and we found a clear example when searching the most stable conformer of complex **2** with the Osawa method.<sup>33</sup> This search yielded a structure 31.7 kcal/mol below that presented above, a structure that is shown in Figure 1 (labeled as **2b**). In this molecule, the palladium atom has an octahedral geometry; the C—N bond has broken (C—N distance: 2.8956 Å), and the carbon atom is also coordinated to the palladium (Pd—N: 1.980 Å; Pd—C: 2.080 Å; Pd—Br: 2.496 Å). The sixth coordination site is occupied by a hydrogen atom from a phenyl ring of the triphenylphosphine (Pd—H: 1.785 Å). This structure is obviously an artifact of the method: single-point DFT calculations at the SVWN level show that this structure is 40.6 kcal/mol higher in energy than the system with the square-planar palladium. Therefore, even in a case like this one where the method seems to work, caution must be always exerted.

## COMPLEXES WITH THE H<sub>2</sub> LIGAND

Dihydrogen complexes are species where a hydrogen molecule is coordinated to a transition metal without breaking of the H—H bond. Their discovery in the 80s represented a small revolution in the world of coordination chemistry.<sup>42–44</sup> They are good candidates for testing of the PM3 (tm) method for at least two reasons. The first of them is that the peculiarity of bonding, with a subtle balance between donation and backdonation, converts dihydrogen complexes in a challenge for molecular orbital methods, and is hardly affordable for molecular mechanics approaches. The second advantage is the existence of a number of theoretical studies on these species,<sup>45</sup> which, as a result, provides a way to rate against them the performance of PM3 (tm). In any case, one must admit that dihydrogen complexes constitute a quite formidable challenge for theoretical methods, and one could expect *a priori*

a poor performance from PM3 (tm). Remarkably enough, this is by no means the case.

Two different families of complexes were tested. One of them is derived from the original system of Kubas,<sup>42</sup> [W(CO)<sub>3</sub>(H<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>] (R = H (**4a**), <sup>*i*</sup>Pr (**4b**), <sup>*t*</sup>Bu (**4c**)); and the other is derived from a complex containing an elongated dihydrogen,<sup>46, 47</sup> [Ru(η<sup>5</sup>-C<sub>5</sub>X<sub>5</sub>)(H<sub>2</sub>)(PR<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)] {R = H, X = H (**5a**); R = H, X = Me (**5b**); R = Ph, X = Me (**5c**)}.

The compound [W(CO)<sub>3</sub>(H<sub>2</sub>)(P<sup>*i*</sup>Pr)<sub>2</sub>] (**4b**) was the first dihydrogen complex, prepared by Kubas et al.,<sup>42</sup> and its molecular structure was determined by both X-ray and neutron diffraction. A number of theoretical calculations have been published on the corresponding model [W(CO)<sub>3</sub>(H<sub>2</sub>)(PH<sub>3</sub>)<sub>2</sub>] (**4a**). Apart from Extended Hückel calculations with no geometry optimization,<sup>48</sup> one can mention two works at the RHF level,<sup>49, 50</sup> and three with nonlocal DFT level methods.<sup>51–53</sup> Geometrical parameters of these earlier geometrical optimizations, as well as those from experiment, are collected in Table III, together with the results of our PM3 (tm) geometry optimizations. Only the geometry of one of the three nonlocal DFT calculations is presented,<sup>52</sup> because the differences with the other two, related to minor changes in the basis sets, are small. Figure 3 presents the PM3 (tm) optimized geometry of **4a**, **4b**, and **4c**.

First, we compared the results of the geometry optimization of **4a** with the three different methods between them and with experimental data on **4b**. All calculations yield a good qualitative description of the compound, with a dihydrogen unit (H—H between 0.796 and 0.909 Å) coordinated to the metal. The computational difference between the two RHF calculations is in the basis set. One of them<sup>49</sup> has a minimal basis set, and the other<sup>50</sup> a valence double- $\zeta$  basis set with polarization functions on the hydrogens. The improvement associated with the extension of the basis set is clear in the W—H distance, the difference with experiment improving from 0.26 to 0.02 Å. The three nonlocal DFT calculations yield results that are also in very good agreement with the experiment, the one presented in Table III showing the correct value for the H—H distance and a difference of 0.04 Å in the W—H distance. Our PM3 (tm) calculation of **4a** fares fairly well in terms of bond distances. The computed H—H distance (0.909 Å) is 0.08 Å larger than experiment, and the W—H distance (1.826 Å) is 0.06 Å shorter. Other bond distances are also well reproduced, and the overall geometry is octahedral, as shown by the P—W—P and C—W—C bond angles near 180°. Finally, the orientation of the H—H

TABLE III.

Comparison between Experimental and Optimized Bond Lengths (Å) and Angles (°) for Complexes  $[\text{W}(\text{CO})_3(\text{H}_2)(\text{PR}_3)_2]$ , with  $\text{R} = \text{H}$  (**4a**),  $i\text{Pr}$  (**4b**),  $t\text{Bu}$  (**4c**).

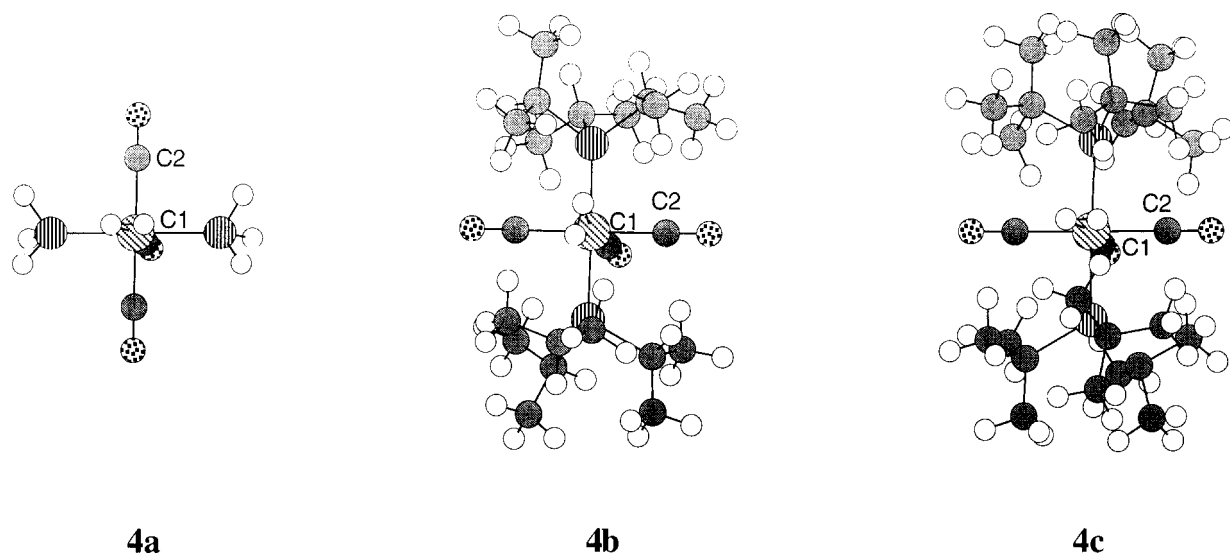
	Exp.- <b>4b</b> <sup>a</sup>	RHF- <b>4a</b> <sup>b</sup>	RHF- <b>4a</b> <sup>c</sup>	DFT- <b>4a</b> <sup>d</sup>	PM3- <b>4a</b>	PM3- <b>4b</b>	PM3- <b>4c</b>
H—H	0.82	0.796	0.812	0.818	0.909	0.861	0.852
X—W	1.84	2.116	1.867	1.891	1.768	1.797	1.792
W—H	1.89	2.153	1.911	1.934	1.826	1.850	1.848 <sup>e</sup>
W—P <sup>e</sup>	2.495			2.469	2.340	2.350	2.409
P—C <sup>e</sup>	1.862			—	—	1.970	2.055
W—C(1)	1.977			1.977	2.032	2.035	2.023
W—C(2) <sup>e</sup>	2.030			2.025	2.039	2.054	2.065
P—W—P	178.3			176.4	178.5	177.4	173.9
C—W—C	175.9			177.5	179.8	177.3	177.3

<sup>a</sup> Data from ref. 42.<sup>b</sup> Data from ref. 49.<sup>c</sup> Data from ref. 50.<sup>d</sup> Data from ref. 52.<sup>e</sup> Average values.

bond is parallel to the P—W—P axis, also in agreement with experiment. In summary, all qualitative features of the geometry of **4a** are well reproduced by the PM3 (tm) calculation, and the quantitative accuracy is comparable to that of a minimal basis RHF calculation.<sup>49</sup>

The low computational cost of the PM3 (tm) calculation allows the introduction of the real substituents in the phosphine, something that is hardly affordable for *ab initio* methods. In this way, we have also computed the experimental system

$[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^i\text{Pr}_3)_2]$  (**4b**), and a hypothetical species  $[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^t\text{Bu}_3)_2]$  (**4c**), where the phosphines are even bulkier. Selected bond distances and angles are also listed in Table III, and the pictures are included in Figure 3. The differences between the PM3 (tm) optimized geometries of **4a**, **4b**, and **4c** are quite small, providing further proof that **4a** is indeed a good model for **4b**. Some trends are nevertheless worth mentioning. For instance, there is a shortening in the H—H distance (0.909, 0.861, 0.852 Å) when going from **4a** to **4c**, coupled to a cer-



**FIGURE 3.** PM3 (tm) optimized geometries of complexes  $[\text{W}(\text{CO})_3(\text{H}_2)(\text{PH}_3)_2]$  (**4a**),  $[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^i\text{Pr}_3)_2]$  (**4b**), and  $[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^t\text{Bu}_3)_2]$  (**4c**).

**TABLE IV.**  
**Comparison between Experimental and Optimized Bond Lengths (Å) and Angles (°) for Complexes**  
**[Ru( $\eta^5$ -C<sub>5</sub>X<sub>5</sub>)(H<sub>2</sub>)(PR<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)], with R = H, X = H (5a); R = H, X = Me (5b); R = Ph, X = Me (5c).**

	Exp.-5c <sup>a</sup>	DFT-5a <sup>b</sup>	PM3-5a	PM3-5b	PM3-5c
H—H	1.08	0.888	1.678	1.678	1.027
Ru—Y <sup>d</sup>		1.657	1.392	1.392	1.600
Ru—H	1.66	1.715	1.625	1.625	1.680
Ru—C(Cp) <sup>c</sup>	2.223	2.315	2.21	2.22	2.20
Ru—P <sup>c</sup>	2.300	2.350	2.257	2.261	2.259
P—Ru—P	71.5	71.8	72.5	72.1	72.8
P—C—P	94.0	94.6	91.0	90.7	90.2
Ru—P—C	97.3	97.5	98.3	98.6	98.3

<sup>a</sup> Data from ref. 47.  
<sup>b</sup> Data from ref. 54.  
<sup>c</sup> Average values.  
<sup>d</sup> is the midpoint of the H—H bond.

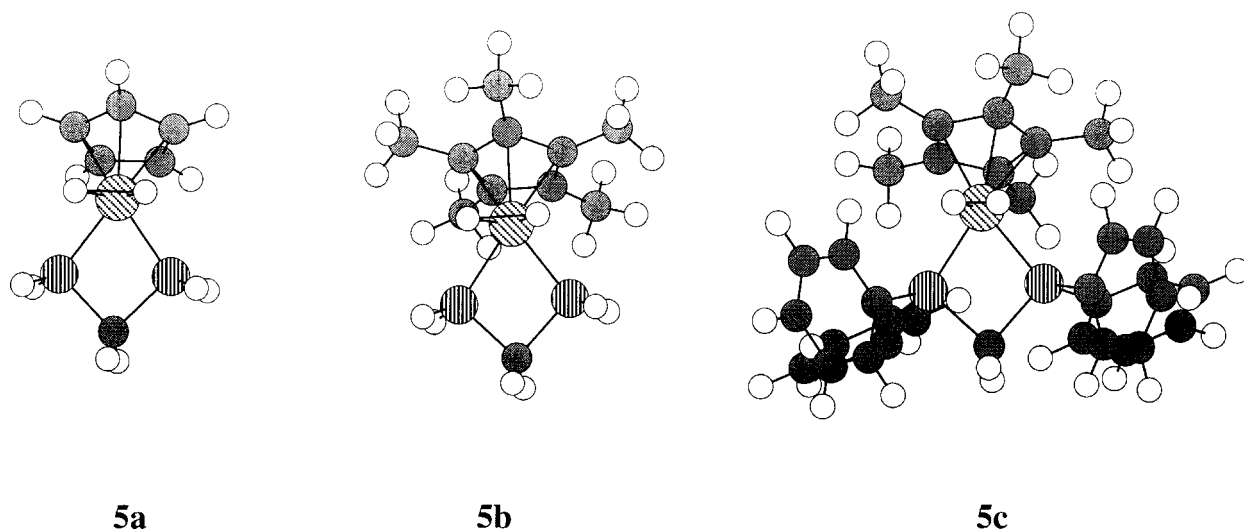
tain lengthening of the W—H distance (1.826, 1.850, 1.848 Å), and also an increase in the W—P distance (2.340, 2.350, 2.409 Å), especially in the case of 4c. There is a rotation of the hydrogen molecule around the W—X (X = center of H—H) axis when going from 4b to 4c, but we cannot ascertain the accuracy of this prediction. All these small changes improve the agreement between the PM3 (tm) results and the experimental structure, but it is difficult to assess their significance because after all, the *ab initio* calculations on 4a already provide a better agreement with the experimental data on 4b.

After the acceptable performance of PM3 (tm) with complexes 4, we decided to submit it to a more demanding test. The geometry reproduction of elongated dihydrogen complexes with H—H in the range 1.0–1.2 Å has proven to be a very elusive target for theoretical calculation, with results hardly getting closer than 0.1 Å from the experiment,<sup>52, 54</sup> often giving dihydride isomers.<sup>45</sup> Because of that, we decided to test PM3 (tm) on species derived from [Ru( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(H<sub>2</sub>)(PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)] (5c). Neutron diffraction data are available for this species from Morris and coworkers,<sup>46, 47</sup> and a recent theoretical study on [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(H<sub>2</sub>)(PH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>)] (5a) has been presented by Gelabert et al.<sup>54</sup> at the nonlocal DFT Becke3LYP level.<sup>54</sup> We have computed the simple theoretical model 5a, the experimental system 5c, and the intermediate model [Ru( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(H<sub>2</sub>)(PH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>)] (5b). The geometrical parameters from these previous experiments and calculations are presented in Table IV together with the results of our PM3 (tm) calculation on species 5a, 5b, and 5c. Figure 4 shows the optimized geometries.

In this case, the difference between the computed structures for 5a and the experimental structure of 5c are important in what concerns the hydrogen coordination to the metal. The DFT computed structure<sup>54</sup> shows a “normal” dihydrogen complex, the H—H distance of 0.888 Å falling 0.20 Å short from the experimental value, a discrepancy that has been partly explained by the quantum vibrational motion of the nuclei.<sup>54</sup> Our PM3 (tm) optimized structure for 5a is, on the other hand, even further from the experimental elongated dihydrogen complex, being clearly a dihydride with an H—H distance of 1.678 Å.

The result of the PM3 (tm) optimization of the species [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(H<sub>2</sub>)(PH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>)] (5b) and [Ru( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(H<sub>2</sub>)(PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)] (5c) hint at an alternative explanation for the experimental structure of 5c. The addition of the methyl substituents on the cyclopentadienyl ring (5b) has practically no effect on the coordination of the hydrogen, but the change upon the addition of the phenyl groups on the phosphine ligands (5c) is dramatic. The PM3 (tm) computed structure for 5c has a H—H distance of 1.027 Å, only 0.05 shorter than the experimental value, that is, substantially better than the DFT value. Other geometrical parameters in Table IV are also very well reproduced. Therefore, these results indicate that the structure is significantly affected by the presence of the phenyl rings on the phosphine ligands, being still unclear from these calculations whether their main effect is electronic or steric.

The PM3 (tm) method therefore provides good quality results in the geometry optimization of the two families of dihydrogen species we have consid-



**FIGURE 4.** PM3 (tm) optimized geometries of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{H}_2)(\text{PH}_2\text{CH}_2\text{PH}_2)]$  (**5a**),  $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{H}_2)(\text{PH}_2\text{CH}_2\text{PH}_2)]$  (**5b**), and  $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{H}_2)(\text{PPh}_2\text{CH}_2\text{PPh}_2)]$  (**5c**).

ered. It is indeed of similar quality, even better in some cases, than much more expensive calculations at *ab initio* levels on model systems. This is especially surprising if one takes into account that PM3 is usually considered to have problems in the calculation of  $\text{H}\cdots\text{H}$  interactions.<sup>55,56</sup> One may wonder if the correction introduced in the PM3 (tm) method for this  $\text{H}\cdots\text{H}$  interaction leads to an accidental success for dihydrogen species. In any case, we can only state here its success for the systems we have tested.

### Coordination of $\text{H}-\text{BR}_2$ $\sigma$ Bonds in Titanium Complexes

The unexpected success of the PM3 (tm) method in the reproduction of the structure of dihydrogen complexes prompted us to probe its performance on yet another case of  $\sigma$  bond coordination to a transition metal. This is the coordination of an  $\text{H}-\text{BR}_2$  bond. The first example of this novel type of complexes has been recently reported by Hartwig and coworkers,<sup>57</sup> and has the form  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{HBcat})_2$  (cat =  $\text{O}_2\text{C}_6\text{H}_4$ ).

In this case, there is the advantage that theoretical results at the MP2 level are available for two different model systems, namely  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{HBH}_2)_2$  (**6a**) and  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2[\text{HB}(\text{OH})_2]_2$  (**6b**).<sup>57</sup> On the other hand, there is the problem that no neutron diffraction data are available, so the experimental location of the hydrogen atoms, based on X-ray data, is not very reliable. We carried out PM3 (tm)

calculations on these two models **6a** and **6b**, as well as on the experimental system  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{HBcat})_2$  (**6c**). Selected geometrical parameters are collected in Table V, and the optimized structures are shown in Figure 5.

Agreement between the MP2 results on **6a** and **6b** with experimental data on **6c** is reasonable, but not perfect. The experimental  $\text{Ti}-\text{B}$  bond distance of 2.335 Å is not far from computed values of 2.385 Å (**6a**) and 2.376 Å (**6b**), but the oscillation of the  $\text{B}-\text{B}$  intramolecular distance is larger (2.11 Å in the X-ray structure of **6c**, 2.019 Å for **6a**, 1.957 Å for **6b**). One can attribute the discrepancies between the MP2 results and the experiment to the modelization and, in fact, the differences between the MP2 optimized structures of **6a** and **6b**, even more apparent in the location of hydrogen atoms, point in this direction.

The internal consistency that is observed in the MP2 results is lost in the PM3 (tm) calculations. The computed  $\text{Ti}-\text{H}$  distance is practically the same for **6a**, **6b**, and **6c** (1.796, 1.805, 1.801 Å) but this is one of the few parameters involved in the  $\sigma$  bond coordination that is conserved in the three geometries. The  $\text{Ti}-\text{B}$  distance increases as much as 0.188 Å when going from **6a** to **6b**, and then decreases by only 0.020 Å when going from **6b** to **6c**. On the other hand, the  $\text{B}-\text{B}$  intramolecular distance oscillates widely, with values of 1.804, 2.394, and 2.232 Å, respectively. In summary, despite the fact that the only major discrepancy between PM3 (tm) optimized structure of **6c** and the X-ray structure is in the  $\text{Ti}-\text{B}$  bond distance (2.455 vs. 2.335 Å), we consider its results for this system to be unreliable, in



**TABLE V.**  
**Comparison between Experimental and Optimized Bond Lengths (Å) and Angles (°) for Complexes**  
**TiCp<sub>2</sub>(H-BR<sub>2</sub>), with BR<sub>2</sub> = B(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub> (6a), B(OH)<sub>2</sub> (6b), and BH<sub>2</sub> (6c).**

	Complex 6a		Complex 6b		Complex 6c	
	PM2 <sup>a</sup>	PM3	PM2 <sup>a</sup>	MP3	Exp. <sup>a</sup>	MP3
Ti—B	2.385	2.287	2.376	2.475	2.335	2.455
Ti—H	1.778	1.796	1.641	1.805	(1.74)	1.801
B—H <sub>μ</sub>	1.303	1.497	1.442	1.539	(1.25)	1.551
B—B	2.019	1.804	1.957	2.394	2.11	2.232
B—Ti—B	50.1	46.4	48.6	57.8	53.8	54.1
H—Ti—H	115.1	123.6	121.8	134.2	(117)	132.2
B—Ti—H	32.5	40.8	36.6	38.2	(32)	39.1
Ti—H—B	100.3	87.5	100.6	95.2	(101)	93.9

Experimental values associated to the unreliable X-ray location of hydrogen atoms are given in parentheses.

<sup>a</sup> Data from ref. 57.

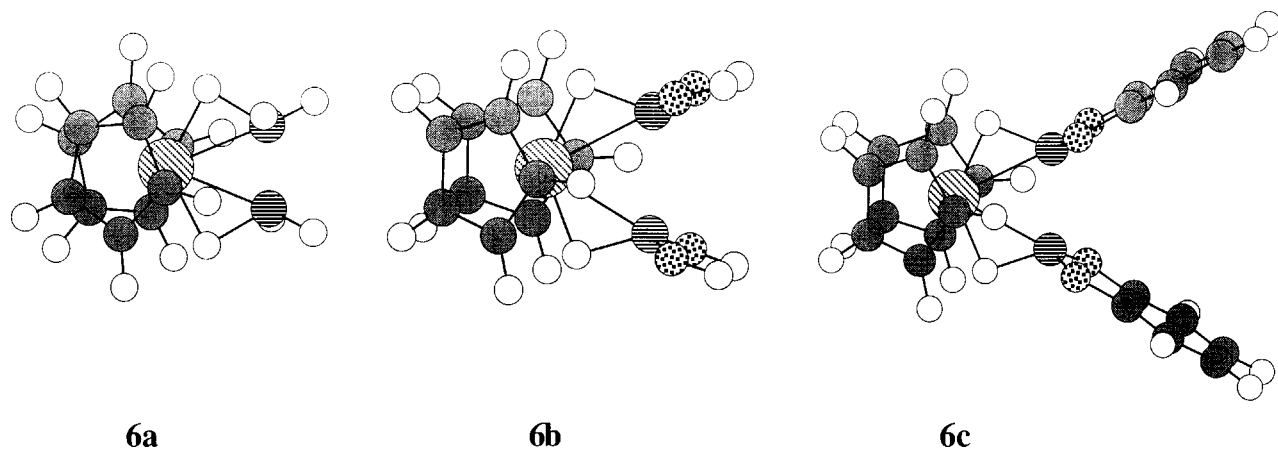
particular in what concerns to the location or the hydrogen atoms.

Thus, we see that the PM3 (tm) method, that yields satisfactory results for the coordination of a  $\sigma$  H—H bond to W and Ru complexes, performs poorly on the coordination of a  $\sigma$  H—BR<sub>2</sub> bond of a Ti complex. At this point, we can only guess at the possible origin of this failure, which could be a poor parametrization of some of the atoms involved, or a peculiarity of this type of complexes.

## Conclusions

The application of the semiempirical PM3 (tm) method to the geometry optimization of different

transition metal systems shows a large variety in the quality of the results. On the positive side, the X-ray geometries of three different cyclometallated complexes ([Pd{C<sub>6</sub>H<sub>4</sub>[CH(Me)NH<sub>2</sub>]}Br(PPh<sub>3</sub>)], [Pd{C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)}Br(PPh<sub>3</sub>)] and [Mn{C<sub>6</sub>H<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>-4,6-CH<sub>2</sub>NMe<sub>2</sub>}(CO)<sub>4</sub>]) are well reproduced, as is also the case for the neutron diffraction geometries of two different dihydrogen complexes ([W(CO)<sub>3</sub>(H<sub>2</sub>)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>], [Ru( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(H<sub>2</sub>)(PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)]). It is especially remarkable the case of [Ru( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(H<sub>2</sub>)(PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)], where the PM3 (tm) calculation on the full system gives better results than far more expensive *ab initio* calculations on the model system. On the negative side, one must mention the erratic behavior on the geometries of the TiCp<sub>2</sub>(HBR)<sub>2</sub> family, and the



**FIGURE 5.** PM3 (tm) optimized geometries of TiCp<sub>2</sub>(HBH<sub>2</sub>)<sub>2</sub> (6a), TiCp<sub>2</sub>[HB(OH)<sub>2</sub>]<sub>2</sub> (6b), and TiCp<sub>2</sub>[HB(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> (6c).

tendency to give very low energy bogus minima on the cyclometallated species. What is particularly disturbing is the contrast between the good results on dihydrogen complexes and the bad results on the seemingly similar H—BR<sub>2</sub>.

In view of the diversity of results, our conclusion on the general reliability of the method can be only mixed. It has a large potential, but its reliability has to be proved on a case by case basis.

## References

- Koga, N.; Morokuma, K. *Chem Rev* 1991, 91, 823.
- Veillard, A. *Chem Rev* 1991, 91, 743.
- Musaev, D. G.; Morokuma, K. *Adv Chem Phys* 1996, 95, 61.
- Jacobsen, H.; Berke, H. *Chem Eur J* 1997, 3, 881.
- Maseras, F.; Morokuma, K. *J Comp Chem* 1995, 16, 1170.
- Matsubara, T.; Maseras, F.; Koga, N.; Morokuma, K. *J Phys Chem* 1996, 100, 2573.
- Dapprich, S.; Komáromi, I.; Byun, K. S.; Morokuma, K.; Frisch, M. J. *J Mol Struct (Theochem)* 1999, 461, 1.
- Dewar, M. J. S.; Thiel, W. *J Am Chem Soc* 1977, 99, 4899.
- Dewar, M. J. S.; Zuehlisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J Am Chem Soc* 1985, 107, 3902.
- Stewart, J. J. P. *J Comp Chem* 1989, 10, 209.
- Thiel, W.; Voityuk, A. *Theor Chim Acta* 1992, 81, 391.
- Thiel, W.; Voityuk, A. *Int J Quantum Chem* 1992, 44, 807.
- Dewar, M. J. S.; Jie, C.; Yu, J. *Tetrahedron* 1993, 49, 5003.
- Holder, A. J. Abstracts of papers of the ACS 1996, 212, COMP 198.
- Ignatov, S. K.; Razuvaev, A. G.; Kokorev, V. N.; Alexandrov, Y. A. *J Phys Chem* 1996, 100, 6354.
- Bacon, A. D.; Zerner, M. C. *Theor Chim Acta* 1979, 53, 21.
- Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg Chem* 1986, 25, 2728.
- Calzaferri, G.; Forss, L.; Kamber, I. *J Phys Chem* 1989, 93, 5366.
- Hehre, W. J.; Yu, J.; Adei, E. Abstracts of papers of the ACS 1996, 212, COMP 092.
- Hehre, W. J.; Yu, J.; Klunzinger, P. E. *A Guide to Molecular Mechanics and Molecular Orbital Calculations in Spartan*; Wavefunction Inc.: Irvine, CA, 1997.
- SPARTAN version 5.0; Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612.
- Cundari, T. R.; Deng, J. *J Chem Inf Comput Sci* 1999, 39, 376.
- Adam, K. R.; Atkinson, I. M.; Lindoy, L. F. *J Mol Struct* 1996, 384, 183.
- Børve, K. J.; Jensen, V. R.; Karlsen, T.; Støvneng, J. A.; Swang, O. *J Mol Mod* 1997, 3, 193.
- Cruz, V. L.; Muñoz-Escalona, A.; Martínez-Salazar, J. *J Polym Sci A* 1998, 36, 1157.
- Dobrowolski, J. C.; Jamroz, M. H.; Kazimirska, J. K.; Bajdor, K.; Borowiak, M. A.; Manna, L.; Miglietta, K. L.; Aresta, M. *Polish J Chem* 1998, 72, 2205.
- Decker, S. A.; Donini, O.; Klobukowski, M. *J Phys Chem A* 1997, 101, 8734.
- Cundari, T. R.; Saunders, L. C.; Sisterhen, L. L. *J Phys Chem A* 1998, 102, 997.
- Pak, J. J.; Weakley, T. J. R.; Haley, M. M. *Organometallics* 1997, 16, 4505.
- López, C.; Bosque, R.; Solans, X.; Font-Bardia, M. *New J Chem* 1998, 977.
- Bosque, R.; López, C.; Solans, X.; Font-Bardia, M. *Organometallics* 1999, 18, 1267.
- Caubet, A.; López, C.; Bosque, R.; Solans, X.; Font-Bardia, M. *J Organomet Chem* 1999, 577, 292.
- Goto, H.; Osawa, S. *J Am Chem Soc* 1989, 111, 8950.
- Vosko, S. H.; Wilk, L.; Nusair, M. *Can J Phys* 1980, 58, 1200.
- Ryabov, A. D. *Chem Rev* 1990, 90, 403.
- Omae, I. *Coord Chem Rev* 1988, 83, 137.
- Newcome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem Rev* 1986, 86, 451.
- Dunina, V. V.; Zaleskaya, O. A.; Potatov, V. M. *Russ Chem Rev* 1988, 57, 250.
- Vicente, J.; Saura-Llamas, I.; Jones, P. G. *J Chem Soc Dalton Trans* 1993, 3619.
- Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G.; Rodríguez de Arellano, M. *Organometallics* 1997, 16, 826.
- Pfeffer, M.; Urriolabeitia, E. P.; Fischer, J. *Inorg Chem* 1995, 34, 643.
- Kubas, G. K.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J Am Chem Soc* 1984, 106, 451.
- Jessop, P. G.; Morris, R. H. *Coord Chem Rev* 1992, 121, 155.
- Crabtree, R. H. *Angew Chem Int Ed Engl* 1993, 32, 789.
- Lin, Z.; Hall, M. B. *Coord Chem Rev* 1994, 135–136, 845.
- Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* 1992, 11, 161.
- Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J Am Chem Soc* 1994, 116, 7677.
- Jean, Y.; Eisenstein, O.; Volatron, F.; Maoche, B.; Sefta, F. *J Am Chem Soc* 1986, 108, 6587.
- Hay, P. J. *J Am Chem Soc* 1987, 109, 705.
- Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J Am Chem Soc* 1990, 112, 2324.
- Li, J.; Ziegler, T. *Organometallics* 1996, 15, 3844.
- Maseras, F.; Lledós, A.; Costas, M.; Poblet, J. M. *Organometallics* 1996, 15, 2947.
- Tomás, J.; Lledós, A.; Jean, Y. *Organometallics* 1998, 17, 190.
- Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *J Am Chem Soc* 1997, 119, 9840.
- Buss, V.; Messinger, J.; Heuser, N. *QCPE Bull* 1991, 11, 5.
- Csonka, G. I. *J Comp Chem* 1993, 14, 895.
- Hartwig, J. F.; Muhoro, C. N.; He, X.; Eisenstein, O.; Bosque, R.; Maseras, F. *J Am Chem Soc* 1996, 118, 10936.